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In-situ preparation of polymer-coated zirconia nanoparticles by decomposition of zirconium-tert-butoxide

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Abstract

Nanocrystalline zirconia particles coated with polymers have been prepared by a two step Chemical Vapor Synthesis process using a hot wall reactor to synthesize the nanocrystalline ceramic core and a subsequent RF plasma reactor for the polymer coating. The polymer coating is built up of organic byproducts of the pyrolysis of the zirconia precursor. By using continuous and pulsed plasma deposition and variation of the plasma parameters, such as RF power, period and duty-cycle, the structure and thickness of the polymer coating can be influenced. Typical particle radii are in the range of 3 to 4 nm with radii of the ceramic core in the range of 2 nm and a coating thickness in the range of 1 to 2 nm. The powders have been characterized by FT-IR, XRD, BET and HRTEM. Consequences for the dispersibility are reported.

Introduction

Nanocrystalline powders are characterized by a very large surface area (of the order of several hundred m^2/g) and surface-to-volume ratio (of the order of 10^8 / m). Therefore, it can be expected that coatings on these ultrafine particles substantially change their characteristics such as chemical reactivity, or catalytic, optical, magnetic and electronic properties[1].

A special field are polymer coated nanocrystalline ceramic particles. The polymer coating could have the function as a spacer to avoid direct contact of the nanoscaled ceramic particles preventing agglomeration[2]. This can have consequences for the dispersibility of treated and untreated nanoparticles in aequous and organic solvents. Furthermore, this preserves special particle properties even after the fabrication of a bulk material, e.g. superparamagnetism in soft magnets[2]. The use of polymer coated nanocrystalline particles as fillers in polymer nanocomposites could be twofold: 1. due to the lack of scattering of visible light the nanocomposite can be transparent even at high volume fraction of nanoparticles; 2. the improvement of the ceramic-polymer interface could result in better mechanical properties.

In this paper the in-situ formation of a polymershell on oxide nanoparticles synthesized by Chemical Vapor Synthesis (CVS) by using a pulsed or continuous plasma is described. The byproducts of the precursor are used for the polymerization. A second route to obtain polymer coatings by using a monomer such as ethene introduced additionally into the plasma reactor will be described in a separate paper[3].

Experimental

The powders are prepared by a modular CVS reactor (Fig. 1), which is similar to assemblies described earlier[3, 4]. It is equipped with a second reaction zone (RF plasma reactor), where the polymer coating takes place. With the first reaction zone, the hot wall reactor, it is

possible to prepare oxide nanoparticles of small grain size (of the order of a few nanometers), narrow size distribution and low degree of agglomeration[4]. Argon gas is bubbled through a container with the zirconia precursor (zirconium-tert-butoxide, ZTB, $Zr(OC_4H_9)_4$) controlled by a MKS thermal mass flow controller (50 sccm). The bubbler is held at a temperature of 75°C by means of a water bath. As the gas flow through the bubbler is not sufficient for maintaining the process pressure of 10 hPa an additional argon gas flow is used (1000 sccm). The first reaction zone consists of an alumina tube with an inner diameter of 19 mm heated by a furnace to 1100°C for the production of zirconia nanoparticles by pyrolysis of ZTB. A mixed flux of argon, organic byproducts of the pyrolysis of ZTB and zirconia nanoparticles enters the plasma reactor which consists of a quartz tube with an inner diameter of 34 mm. The electric field generating the plasma is supplied by two electrodes. A stainless steel rod is used as power electrode in the center of the tube. A flexible copper tape is wrapped several times around the tube acting as mass electrode. The high frequency alternating electric field (13.56 MHz) is generated by a RF-Generator. In addition a so called matchbox is used for minimizing the power reflected by the plasma. The pulses are generated by an arbitrary function generator which is connected to the RF-Generator. The ultrafine particles act as seeds for the heterogeneous formation of the polymer films. The coated nanoparticles are separated from the gas stream by thermophoresis due to a thermal gradient between the hot quartz lamps and the water cooled wall of the collecting zone. The pumping unit consists of a sliding vane pump.

Nanoparticles are collected at two different positions in the system. Most powder is deposited in the collecting zone after both reaction zones (position 2). Due to the temperature gradient between the hot wall and the plasma reactor, a small amount of zirconia particles is deposited in the components between the hotwall and the RF plasma reactor (position 1). These powders, which had no contact with the plasma were used as a reference for the modified powders. The powders collected have a very low tap density similar to aerogels[5]. The production rate of the laboratory reactor is about 0.5 to 1g per hour at a yield of about 40%. Most probably the yield is limited by the collection efficiency of the thermophoretic collector.
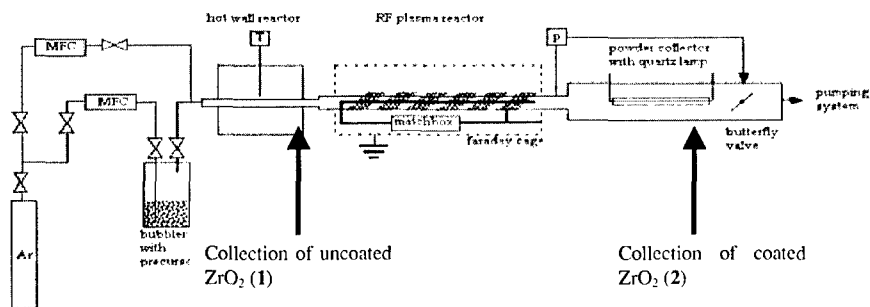

Figure 1: CVS apparatus for the production of polymer-coated nanopowders. The arrows indicate the positions 1 and 2 where uncoated and coated powders were collected, respectively.

The powders were examined by infra-red spectroscopy (Perkin-Elmer 1750) in the range between 4000-400 cm^{-1} and by X-ray diffraction (STOE STADI P) using Ni-filtered Cu-Kα radiation. The specific surface area of the powder was measured by nitrogen absorption with a

Quantachrom Autosorb-3B instrument. High resolution transmission electron microscopy (HRTEM) micrographs were obtained using a Philips CM20 microscope operated at 200 kV.

Results and Discussion

Metal oxide nanopowders are usually prepared using CVS by decomposition of a metal alkoxide precursor in a mixture of an inert gas and oxygen,[5] where the oxygen is used to reduce the amount of carbonaceous impurities in the product. However, it is evident that for the deposition of polymers in the plasma reactor free oxygen which would oxidize the monomer has to be absent. Therefore, an additional oxygen gas flow cannot be used to prepare the zirconia nanoparticles. Fortunately, stochiometric ZrO_2 is can be prepared by pyrolysis of zirconium-t-butoxide ($Zr(OC_4H_9)_4$) in the hot wall reactor according to the reaction.

$$Zr(OC_4H_9)_4) -> ZrO_2 + 2\text{-butanol} + \text{butene} + \text{water} + \text{other byproducts.} \qquad (1)$$
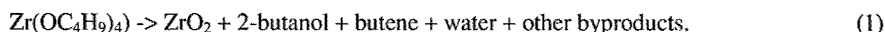
In our new approach the byproducts, such as butanol and especially butene are used as monomers for the deposition of the polymer coating. Uncoated zirconia particles were collected at position **1** in the reactor and plasma treated zirconia at position **2** as indicated in figure 1. Different conditions were employed in the plasma zone: continuous plasma, pulsed plasma with different frequencies and duty cycles. Table 1 summarizes the different conditions. The values of the average power are calculated by equation (2), with $t_{on}/(t_{on} + t_{off})$ corresponding to the duty cycle [6].

$$P_{av} = P_P * \frac{t_{on}}{\left(t_{on} + t_{off}\right)} \qquad (2)$$

X-ray diffractograms of the powders (Fig. 2) show the formation of crystalline ZrO_2 in the tetragonal phase. However, due to the line broadening, it is not possible to distinguish it definitely from the cubic phase at these small grain sizes. The coated powders collected at position **2** after passing the plasma zone have a yellow colour which is typical for polymer coated nanopowders[3]. The yellow tone gets more and more intense with increasing average power. Powders prepared using a continuous plasma (A) are dark yellow and the particles coated under conditions C are slightly yellow coloured. The zirconia powders collected at position **1** is white.

Table I: Plasma parameters of the experiments

	Peak Power [W]	Pulse on [ms]	Pulse off [ms]	Period [ms]	Duty Cycle [%]	Average Power [W]
A (cont.)	47	-	-	-	-	47
B (pulsed)	105	10	30	40	25	26,3
C (pulsed)	99	1	39	40	2,5	2,5
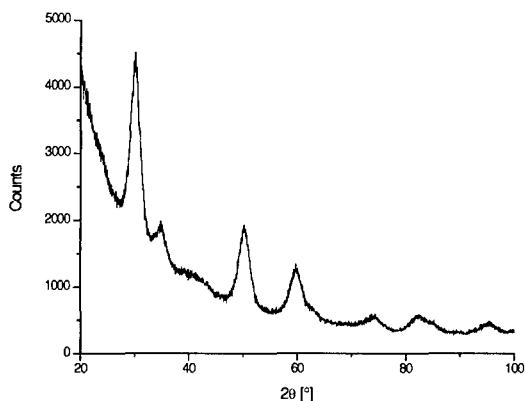
Figure 2: XRD diffractrogram of zirconia powder coated with polymer

Zirconia nanoparticles collected from position **2** from experiments without any plasma do not show any absorption bands in the ranges from 1350-1500 cm^{-1} and 2850-3000 cm^{-1}. Zirconia nanoparticles from position **1** from the plasma experiments (condition A, B, C) are almost identical to that pure zirconia. There are small differences in the range from 1350-1500 cm^{-1} due to small amounts of organic adsorbants (not shown). Figure 3 shows IR spectra of different zirconia nanopowders coated under conditions A, B, C and collected at position **2**. It is clearly visible that new absorption bands develop in the plasma zone which get more and more intense with increasing average plasma power. These bands can be attributed to C-H stretching vibrations (2956 cm^{-1}, 2932 cm^{-1} and 2870 cm^{-1}) and to CH_2 and CH_3 groups bending vibrations (1456 cm^{-1} and 1378 cm^{-1}), which are typical for plasma polymers out of hydrocarbon monomers [7]. The adsorption bands at 1576 cm^{-1} and at 1626 cm^{-1} originate from carboxylate groups and physisorbed water, respectively[8], and are found in spectra of other ceramic nanoparticles prepared under these conditions, too [3].
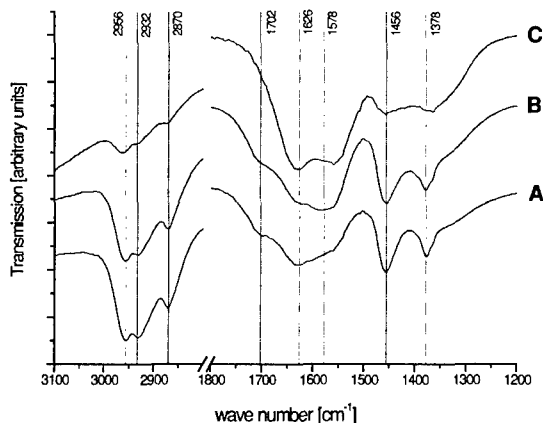
Figure 3: FTIR spectra of plasma treated zirconia powders collected at position 2 (coated) prepared under A) continuous plasma B) pulsed plasma 10/30 and C) pulsed plasma 1/39

The shoulder at 1702 cm^{-1} in the spectra A and B is due to carbonyl stretching vibrations. The IR spectra clearly show that the amount of polymer produced next to the zirconia nanoparticles increases with increasing average plasma power.

The evidence of the coating of the nanoparticles is gained from the HRTEM micrographs in Figure 4. The micrographs are taken from two powders collected at the positions 1 (left) and 2 (right) prepared under the conditions A. In the left micrograph crystalline, non-spherical particles with lattice fringes up to the particles surfaces can be detected. The crystalline particles in the right micrograph are embedded in an amorphous matrix, which is interpreted to be the polymer detected in the IR-spectrum. Again, all particles collected at position 1 result in similar TEM-micrographs even if the experiment was performed under conditions B or C. However, the micrographs of particles from position 2 differ from the right micrograph shown here. Particles prepared under condition B have only very thin amorphous layers (micrograph not shown). On micrographs of powder from the condition C experiment no amorphous areas were detected (not shown), although some polymer bands are visible in the IR-spectrum of these particles.

Table 2 gives an overview of different grain sizes and particle sizes calculated from XRD line broadening (Scherrer formula) and nitrogen adsorption (BET), respectively. The particle sizes at position 1 are in the same order of the grain sizes derived from the XRD. They are all smaller than the particles at position 2.

The plasma treatment changes the macroscopic properties of the nanoparticles such as dispersibility and wetting behaviour. The zirconia from position 1 is dispersable in acidic water (pH-value 2) to 80 nm (not shown). However, the plasma treated powder of the experiments A and B is not wettable in water, but in acetone or ethanol. Unfortunatly, the dispersibility is lost. The powder prepared under the C-conditions is dispersable in acidic water, but only to 140 nm. A continuous plasma (A) forms thick polymer coatings around the zirconia nanoparticles which let the particles loose their hydrophilic character. Under pulsed conditions with a medium average power (B) a thin (nearly invisible in TEM micrographs) polymer shell is deposited on the particles. However, this coating is sufficient to change the dispersibility of the particles completely. The particles prepared under conditions C show nearly no differences in the TEM micrographs and dispersibility compared to untreated zirconia, although the colour of the particles and the IR spectra indicates small amounts of polymer.

Table II: Grain size (diameter) of zirconia and polymer coated zirconia determined from XRD line broadening and nitrogen adsorption (BET) for the different experimental conditions

	C (pulsed plasma)	B (pulsed plasma)	A (continuous plasma)
Grain Size (XRD) [nm]	3,8	3,9	3,9
Particle Size Position 1 (BET) [nm]	4,5	4,8	4,1
Particle Size Position 2 (BET) [nm]	4,7	6,1	4,8
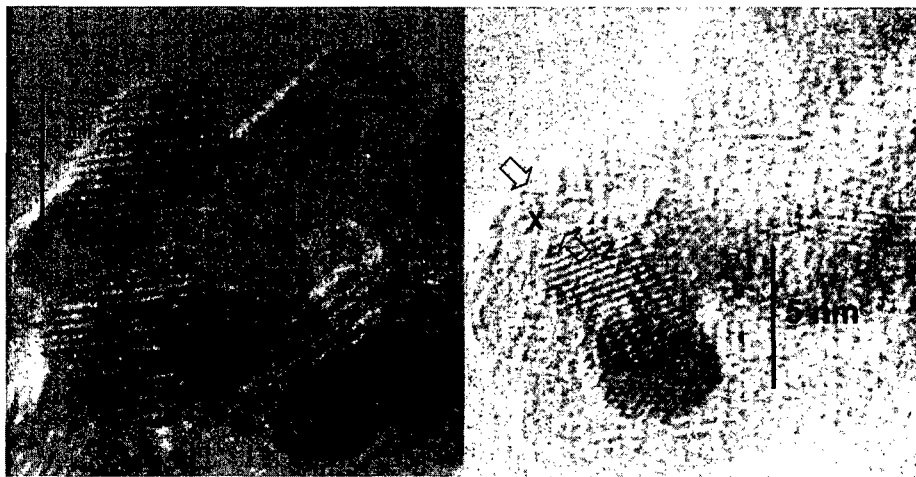
Figure 4: Transmission electron micrographs of powders collected at position **1** (left) and **2** (right) prepared under conditions A. The markers indicate a shell structure X around a core Z.

Conclusions

From the combined results of FTIR, XRD, BET and TEM experiments it is concluded that the plasma polymerization of the pyrolysis byproducts of the zirconia precursor leads to a polymer coating of the zirconia nanoparticles without the addition of any monomer. The thickness of the coatings depends on the plasma parameters and decreases with decreasing average power, adjustable by using continuous and pulsed plasmas with variable duty cycles.

This result has important consequences for the functionalization of ceramic nanoparticles. If additional monomers with functional groups are used in the plasma polymerization , the role of the byproducts of the monomer pyrolysis, forming a polymer shell itself, has to be considered.

Acknowledgement

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Poster Session